Methyl Chloride via Oxyhydrochlorination of Methane

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Abstract

Dow Corning is developing a route from methane to methyl chloride via oxyhydrochlorination (OHC) chemistry with joint support from the Gas Research Institute and the Department of Energy Federal Energy Technology Center. Dow Corning is the world's largest producer of methyl chloride and uses it as an intermediate in the production of silicone materials. Other uses include production of higher hydrocarbons, methyl cellulose, quaternary ammonium salts and herbicides. The objective of this project is to demonstrate and develop a route to methyl chloride with reduced variable cost by using methane instead of methanol raw materials.

Methyl chloride is currently produced from methanol, but U.S. demand is typically higher than available domestic supply, resulting in fluctuating prices. OHC technology utilizes domestic natural gas as a feedstock, which allows a lower-cost source of methyl chloride which is independent of methanol. In addition to other uses of methyl chloride, OHC could be a key step in a gas-to-liquid fuels process. These uses could divert significant methanol demand to methane.

A stable and selective catalyst has been developed in the laboratory and evaluated in a purpose-built demonstration unit. Materials of construction issues have been resolved and the unit has been run under a range of conditions to evaluate catalyst performance and stability.

Many technological advances have been made, especially in the areas of catalyst development, online FTIR analysis of the product stream, and recovery of methyl chloride product via an absorber/stripper system. Significant technological hurdles still remain including heat transfer, catalysts scaleup, orthogonality in modeling, and scaleable absorption data. Economics of the oxyhydrochlorination process have been evaluated and found to be unfavorable due to high capital and utility costs. Future efforts will focus on improved methane conversion at high methyl chloride selectivity.

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Introduction

The silicone industry utilizes methyl chloride in the direct process in a reaction with silicon to form $(CH_3)_2SiCl_2$ which is then hydrolyzed to form silicones. Methyl chloride is conventionally produced in a reaction between methanol and HCl. However, the high price and volatility of the price of methanol make it desirable to produce methyl chloride via an alternate route (see Figure 1).

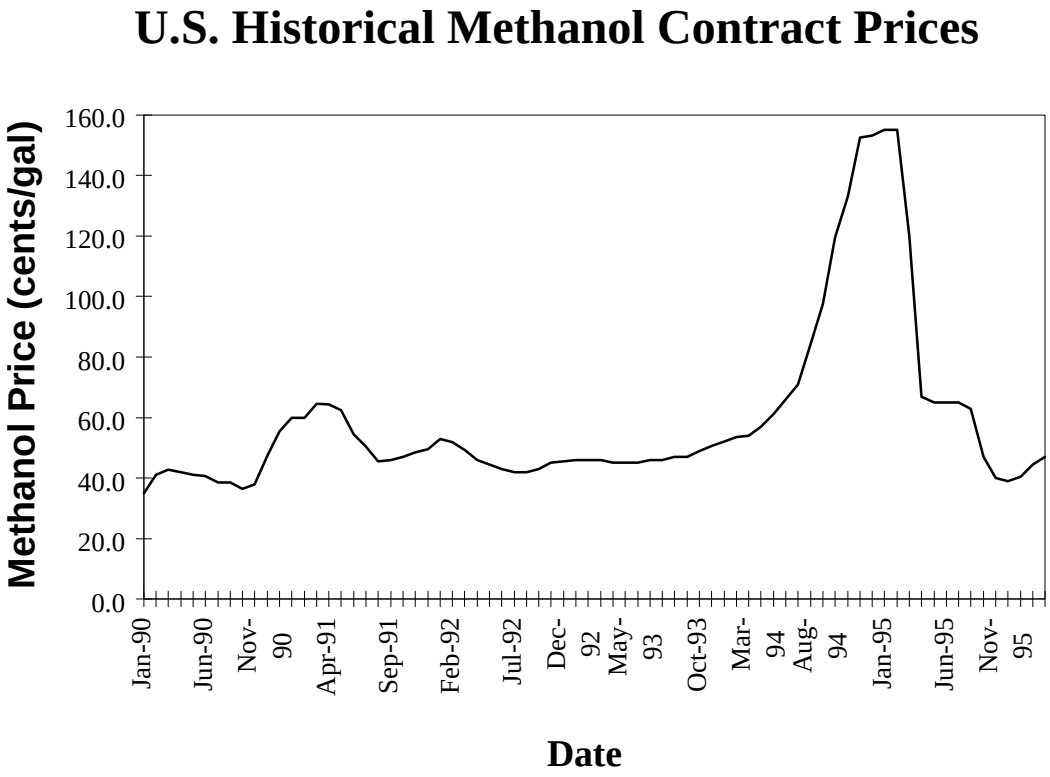

Figure 1. U.S. Historical Methanol Prices versus date since 1990. The spike in prices at the end of 1994 is due to production of methyl-tert-butyl ether (MTBE).

Dow Corning Corporation has been investigating producing methyl chloride via oxyhydrochlorination (OHC) of methane. This chemistry and other associated chemistries are shown in Table 1.

Table 1. Oxyhydrochlorination Chemistries

Primary Reaction	ΔE(kJ/Mol)	ΔH(kJ/Mol)
$CH_4 + HCl + 1/2\ O_2 \longrightarrow CH_3Cl + H_2O$	121	-157
Subsequent Chlorination Reactions		
$CH_3Cl + HCl + 1/2\ O_2 \longrightarrow CH_2Cl_2 + H_2O$	126	-153
$CH_2Cl_2 + HCl + 1/2\ O_2 \longrightarrow CHCl_3 + H_2O$	126	-153
Combustion Reactions		
$CH_4 + 3/2\ O_2 \longrightarrow CO + 2\ H_2O$	225	-500
$CH_4 + 2\ O_2 \longrightarrow CO_2 + 2\ H_2O$	240	-781
$CH_3Cl + O_2 \longrightarrow CO + H_2O + HCl$	187	-343
$CH_3Cl + 3/2\ O_2 \longrightarrow CO_2 + H_2O + HCl$	197	-624

Oxyhydrochlorination, which produces methylene chloride in addition to methyl chloride, is a potential beginning to a gas-to-liquid fuels process. This chlorohydrocarbon mixture can be oligomerized to form liquid hydrocarbon fuels.[1,2]

Results and Discussion

Economics

The completion of Dow Corning's evaluation of the OHC route to methyl chloride in the process development unit has lead to a more complete evaluation of the economics of the process. Some savings are realized due the lower cost of methane versus methanol. However, the process has been found to be economically unfavorable overall. This is due to capital and utility costs much greater than conventional technology. Since beginning the research into the OHC technology, gains have continued to be realized with conventional routes to methyl chloride both due to technological advances and to increases in the economy of scale. The bottom line is that the OHC route to methyl chloride is not economically favorable. However, many technological advances have been made and are detailed in the remainder of this paper.

Catalyst Technology

As previously reported, a stable and selective catalyst was developed for the production of methyl chloride from methane.[3] This catalyst contains copper, lanthanum, and lithium supported on alumina. Copper was found to be the best catalyst for the OHC chemistry. Lanthanum promotes the activity of a copper based catalyst. Lithium increases the stability of a catalyst containing copper and lanthanum. Designed experimentation reinforced this selection of metals with a positive response for the three factor interaction of copper, lanthanum, and lithium. Finally, alumina was chosen as the support because it formed a very stable catalyst due to strong metal to support interactions. Silica supported catalysts showed slightly better conversions/selectivities, but unacceptable stability. Mixed zirconia/alumina supported catalysts were not chosen because of lower methyl chloride selectivity due to higher support acidity causing increased combustion of reactants and products.

Reactor Technology

The reactor used in the process development was a shell and tube reactor consisting of 19 0.5" x 72" tubes with enough heat transfer area to tolerate a heat duty of up to 95,750 Btu/h. This reactor was intended to draw the excess heat out of the highly exothermic OHC chemistry to allow isothermicity and easy control of the process. However, this did not prove to be the case. Large axial and radial temperature gradients (10-20°C) were observed. This complicated process control and interpretation of results. In the end, after much designed experimentation, reactor temperature was concluded to be the most important factor in the process. Attempts were made to eliminate the temperature gradients with catalyst dilution. Dilution of the alumina supported catalyst with virgin alumina only made the problem worse. The acidic alumina increased the amount of combustion in the process and therefore, temperature gradients were worse. Diluting the catalyst bed with glass beads was, however, successful to some extent. Temperature gradients were lessened, and at lower reactor temperatures (300-340°C) isothermicity was approached. However, this approach was unsuccessful at greater than 340°C. Heat transfer proved to be the most critical issue encountered in the process development unit.

Product Analysis Technology

Analysis of the products from OHC technology was a critical issue for the process development unit. It was hoped that a method could be found to allow real time control of the unit. In addition to quick data collection, a very complicated stream of greater than ten components was being produced. This analysis was accomplished using an online KVB/Analect PCM-5000 FTIR with silicon windows. Initial attempts to use the recommended AMTIR (Amorphous Material Transmitting Infrared Radiation) windows failed due to quick corrosion upon exposure to the product stream. However, silicon windows showed no evidence of corrosion even after nine months of use in the process development unit. Once data could be collected through the silicon windows, sophisticated mathematical modeling techniques were needed to deconvolute the data.

Inverse least squares regression methods were used to quantify CO, CO2, C2H6, C3H8, HCO2H, and H2O. Partial least squares regression analysis was used for CH4, HCl, CH3Cl, CH2Cl2, CHCl3, and CCl4.

Absorber/Stripper Technology

Upon exiting the reactor, the product stream entered the absorber for removal or chlorohydrocarbons. The absorber consisted of a 4"x192" glass-lined column packed with 3/4" porcelain Intalox saddles. This system demonstrated the capability to remove 99+% of the CH3Cl from the product stream. Water and other chlorohydrocarbons were also collected in a phase separator at the bottom of the absorber column. The chlorohydrocarbon/absorber solvent phase was then fed to a stripper column where the chlorohydrocarbons were stripped overhead away from the solvent. The stripper consisted of a 4"x120" PFA-lined column packed with 3/4" porcelain Intalox saddles. 99+% removal of chlorohydrocarbons from solvent was demonstrated.

Technological Hurdles

Although process economics discourage further research on this technology, a number of technological issues have been identified for development, including heat transfer, catalyst scaleup, and orthogonality in product stream analytical modeling. However, if higher methane conversions with high selectivity to methyl chloride could be maintained with high conversion of HCl, the basic route to methyl chloride from methane still looks promising.

Heat transfer is by far the most important issue encountered in this technology. The inability to remove heat from the system causes the exothermic OHC chemistry to initiate combustion of both reactants and products. Combustion reactions are even more exothermic, and a runaway situation soon follows. Even if runaway reactions can be prevented, process control is difficult and inaccurate due to non-isothermicity of the catalyst bed. Interpretation of results is also very much complicated by the lack of an isothermal process.

Catalyst scaleup with a catalyst manufacturer needs to be more thoroughly pursued. Three different rounds of catalyst production each yielded improved results, but still could not equal the performance of catalyst produced in the laboratory.

Even though a precision of 5-15% relative standard deviation was achieved with online FTIR analysis, modification of select mathematical models is recommended. This will insure orthogonality between absorption bands of individual stream components. Measurable concentration ranges for CH_4 and HCl should also be increased to allow more flexibility in process parameters. Measuring the feed composition by FTIR as well as the product distribution will also increase the accuracy of the calculated conversions and selectivities.

Conclusions

Although significant technological advances have been made in the areas of catalyst development, product stream analysis with online FTIR, and product recovery using an absorber/stripper system, technological hurdles still remain including heat transfer, catalysts scaleup, orthogonality in modeling, and scaleable absorption data. In the end, however, the most important factor to be considered is the economics of the oxyhydrochlorination route to methyl chloride. High capital and utility costs make this technology economically unfavorable at the present time, and future studies should focus on increased methane conversion at high methyl chloride selectivity to overcome these drawbacks.

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